Cadmium and phosphate in coastal Antarctic seawater: implications for Southern Ocean nutrient cycling

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1 Abstract

Cadmium is a biologically important trace metal that co-varies with phosphate \( (\text{PO}_4^{3-}) \) or Dissolved Inorganic Phosphate, DIP) in seawater. However, the exact nature of Cd uptake mechanisms and the relationship with phosphate and other nutrients in global oceans remains elusive. Here, we present a time series study of Cd and \( \text{PO}_4^{3-} \) from coastal Antarctic seawater, showing that Cd co-varies with macronutrients during times of high biological activity even under nutrient and trace metal replete conditions. Our data imply that Cd/\( \text{PO}_4^{3-} \) in coastal surface Antarctic seawater is higher than open ocean areas. Furthermore, the sinking of some proportion of this high Cd/\( \text{PO}_4^{3-} \) water into Antarctic Bottom Water, followed by mixing into Circumpolar Deep Water, impacts Southern Ocean preformed nutrient and trace metal composition. A simple model of endmember water mass mixing with a particle fractionation of Cd/P \( (\alpha_{\text{Cd-P}}) \) determined by the local environment can be used to account for the Cd/\( \text{PO}_4^{3-} \) relationship in different parts of the ocean. The high Cd/\( \text{PO}_4^{3-} \) of the coastal water is a consequence of two factors: the high input from terrestrial and continental shelf sediments and changes in biological fractionation with respect to P during uptake of Cd in regions of high Fe and Zn. This implies that the Cd/\( \text{PO}_4^{3-} \) ratio of the Southern Ocean will vary on glacial-interglacial timescales as the proportion of deep water originating on the continental shelves of the Weddell Sea is reduced during glaciations because the ice shelf is pinned at the edge of the continental shelf. There could also be variations in biological fractionation of Cd/P in the surface waters of the Southern Ocean on these timescales as a result of changes in atmospheric inputs of trace metals. Further variations in the relationship between Cd and \( \text{PO}_4^{3-} \) in seawater arise from changes in population structure and community requirements for macro- and micronutrients.
Keywords: cadmium, phosphate, coastal, nutrients, Southern Ocean

2 Introduction

Major nutrients (macronutrients) carbon (C), nitrate (NO$_3^-$), phosphate (PO$_4^{3-}$) and, in the case of siliceous organisms, silicic acid (Si or Si(OH)$_4$), are taken up into the organic and skeletal material of marine phytoplankton in the euphotic zone, repackaged by zooplankton and exported as dead cells and fecal pellets. Over 86% of the carbon flux at 100 m is remineralised by 1000 m depth, such that macronutrients exhibit characteristic vertical gradients (Martin et al., 1987). In addition to these macronutrients, trace amounts of other elements (micronutrients) are essential for phytoplankton growth. Although studies into micronutrient biogeochemical cycling have focused on Fe availability, other metals, such as Cd, may be biologically important. Cd is a labile nutrient associated with organic matter and has similar spatial distribution patterns to PO$_4^{3-}$ in open ocean deep and surface waters (Boyle, 1988; Figure 1). The exact nature of the relationship between Cd and P has been discussed extensively in the literature, and has been modelled either as a combination of two linear relationships separated by a “kink” at ~1.3 μmol kg$^{-1}$ PO$_4^{3-}$ as a result of basin specific processes (Cullen, 2006; de Baar et al, 1994; Frew and Hunter, 1992; Yeats, 1998) or a non-linear fractionation curve (Elderfield and Rickaby, 2000).

There is increasing evidence that Cd is a biologically important trace metal, actively taken up by phytoplankton in productive surface waters. Firstly, Cd is known to substitute into the metalloenzyme Carbonic Anhydrase (CA), which catalyses the uptake of bicarbonate (HCO$_3^-$) from seawater providing a source of inorganic C for photosynthesis i.e. the Carbon Concentrating Mechanism or CCM (Morel and Price,
Cd may substitute for Zn in CA such that Cd added to Zn-limited diatoms leads to an increase in cellular CA activity and growth rate (Lane and Morel, 2000; Lee and Morel, 1995; Morel et al., 1994; Price and Morel, 1990). Recent sequencing and primary characterisation has confirmed the presence of a Cd specific CA, i.e. Cd-CA; (Lane et al., 2005; Xu et al., 2008). Cd has also been implicated in the formation of Polyphosphate Bodies (PPBs) in the giant kelp, *Macrocystis pyrifera*. PPBs are ubiquitous to most organisms, and may be active in phytoplankton (Hunter and Boyd, 1997). Secondly, recent seawater analyses have shown that Cd isotopic fractionation occurs in seawater, with the greatest fractionation occurring in surface waters depleted in dissolved Cd suggesting a biological signature (Lacan et al., 2006; Ripperger et al., 2007).

Biological uptake, and thus changes in nutrient demands due to variations in environmental conditions and population structure, could have a significant impact on the relationship between Cd and P in seawater. In addition to providing insight into modern biogeochemical cycling, understanding the relationship between macro- and micronutrients has implications for the reconstruction of past PO$_4^{3-}$ utilisation using Cd/Ca ratios in foraminiferal calcite, which relies on a predictable Cd/PO$_4^{3-}$ ratio in seawater (Boyle, 1986; Rickaby & Elderfield, 1999; Elderfield & Rickaby, 2000). The chemistry of deep water masses could be influenced by continental shelf and coastal processes at the site of formation. Further, past changes in continental shelf inputs to deep water could impact past deep water Cd/PO$_4^{3-}$, and, consequently, the interpretation of benthic foraminiferal Cd/Ca ratios. Here, we investigate the seasonal uptake of Cd and macronutrients in a coastal environment off the West Antarctic Peninsula. We discuss our results in the context of Southern Ocean processes on a
wider spatial scale, and the implications of our results for seawater $\text{Cd/PO}_4^{3-}$ over longer timescales.

3 Methods and materials

3.1 Field setting

Coastal seawater samples were collected from Ryder Bay, which forms the larger part of Marguerite Bay off Adelaide Island, near Rothera Research Station (British Antarctic Survey, BAS), West Antarctic Peninsula (WAP; Figure 2). As well as being ideally located in a climatically sensitive region (Meredith et al., 2004), this site is part of several long term monitoring projects (Clarke et al., 2008; Meredith et al., 2008; Smith et al., 1999). The Rothera Oceanographic and Biological Time-Series (RaTS) has been conducted by BAS since late 1997, following the end of the successful long term monitoring series at Signy, northern WAP, in 1994. Conductivity-Temperature-Depth (CTD) profiles, nutrient analysis and size fractionated pigment assays (to monitor biomass) are carried out on a regular basis throughout the year and further details are reported elsewhere (Clarke et al., 2008).

The Antarctic Circumpolar Current (ACC) pumps nutrient rich, oxygen poor, warm water from the Upper Circumpolar Deep Water (UCDW) onto the continental shelf along the WAP below 200 m and into Marguerite Bay several times a year (Meredith et al., 2004). Vertical mixing of this water occurs largely as a result of bathymetric features and is the principal heat transfer process at depth. Above 100-150 m, the highly seasonal Antarctic Surface Water (ASW) dominates in shelf waters, including Marguerite Bay. In the summer months, the surface water is separated from deeper
water by a strong pycnocline, which develops as a result of warming and freshening and can be defined by a Mixed Layer Depth (MLD). This pycnocline isolates a remnant of the water column, which is well mixed in winter, termed the Winter Water Mass (WW) (Clarke et al., 2008; Meredith et al., 2008; Meredith et al., 2004).

3.2 Field methods

Water column samples were collected 2-3 times a week from January to March in 2005 and 2006 at the RaTS site (Figure 2). The samples were collected from 15 m, the average chlorophyll maximum in Ryder Bay (Clarke et al., 2008), filtered using 0.2 μm polycarbonate membranes (Whatman), acidified to pH 1.7-1.9 using sub-boiling quartz distilled HNO$_3$ under trace metal clean conditions and stored at 4°C. All plasticware used during collection, filtration and analysis was acid-cleaned by soaking in 1 N HNO$_3$ (AnalaR) for at least 24 hours and rinsing thoroughly in 18 MΩ cm Milli-Q water. Laboratory blanks of 18 MΩ cm Milli-Q water were run through the complete protocol outlined to test for contamination in the laboratory.

Additional samples were filtered for silicic acid and phosphate analysis. Glass fibre filters (Whatman GF/F; nominal pore size 0.8μm) are routinely used to filter seawater for N and P analysis. Silica free polycarbonate 0.2 μm filter membranes (Whatman) were used to filter seawater for silicic acid (Si) analysis to avoid contamination by any Si released from the glass fibres of the GF/F membranes. Samples for NO$_3^-$ and PO$_4^{3-}$ analysis were stored at -20°C; samples for silicic acid analysis were stored at 4°C.

3.3 Laboratory methods

i) Initial Cd determinations by standard addition
Approximate trace metal concentrations were measured on a Perkin Elmer Elan 6100DRC Quadrupole Inductively Coupled Plasma Mass Spectrometer (Q-ICP-MS) using a standard addition method. Five aliquots of acidified seawater were diluted ten-fold with 1% sub-boiling quartz-distilled HNO₃ and added to incremental amounts of spike solutions (Greyhound Chromatography). A machine blank was initially run for each batch of five solutions. Pulse intensity was measured six times for each aliquot, the mean value corrected for isobaric interferences and machine blank, and sample concentration calculated by regression.

Cd intensities were measured using¹¹⁴Cd (28.73% natural Cd). Isobaric interference from¹¹⁴Sn (0.65% natural Sn) was corrected for by measuring¹¹⁸Sn, and⁹⁸Mo¹⁶O⁺ was corrected for by monitoring⁹⁸Mo intensities.⁹⁸Mo¹⁶O⁺/⁹⁸Mo⁺ formation in the plasma is 0.2 to 0.4%. The external precision and accuracy were assessed using two independent seawater standards (Table 1). These approximate concentrations were used to determine the optimal quantities of Cd spike that were to be added to the samples, to avoid large error magnification factors in the application of the isotope dilution method. Laboratory blanks were also measured by standard addition, and were below the Limit of Detection (LoD for Cd ~ 0.01 ppb).

**ii) Isotope dilution method**

The small variations in Cd concentrations during the 2006 austral summer were subsequently measured by single-spike isotope dilution after pre-concentration of Cd by Mg(OH)₂ co-precipitation (Wu and Boyle, 1997). An appropriate amount of spike, which had been previously calibrated (Ripperger and Rehkämper, 2007a; Ripperger and Rehkämper, 2007b), was weighed into Teflon containers. Error magnification was reduced by keeping the sample-to-spike mass ratio for Cd approximately equal to
unity. As the co-precipitation method is pH sensitive, the concentration and acidity of
the spike were adjusted after weighing. Approximately 13 ml of acidified seawater
was weighed in 15 ml acid-cleaned polypropylene centrifuge tubes (5 point balance ±
0.01 mg) and spiked with 400 μl of enriched $^{110}$Cd spike solution was added.
Previous experiments have shown that the equilibration is rapid, and there is no
significant difference between samples equilibrated for 2 minutes and 2 days (Wu and
Boyle, 1997). FEP distilled aqueous NH$_3$ (500-2000 μl) was added to precipitate
Mg(OH)$_2$; the amount added was determined empirically to allow ~ 7% Mg to
precipitate to minimise matrix effects during analysis (Mg ~ 1000 ppm; (Wu and
Boyle, 1997)). Cd is preferentially taken up into the precipitate, resulting in ~ 30%
Cd yields. After NH$_4$OH addition, the sample was left for two minutes before
centrifugation at 6000 rpm for 4 minutes. The supernatant was discarded and the
precipitate was redissolved in 0.5 ml 5% HNO$_3$ (sub-boiling distilled HNO$_3$ in Milli-
Q water), diluted with 0.5 ml Milli-Q and analysed for Cd isotopes by ICP-MS.
The standards and samples were analysed using an Element II magnetic sector ICP-
MS (Thermo Finnigan), introduced in conjunction with a Cetac ASX-100
microautosampler. The ICP-MS was run in low resolution mode to optimise counting
statistics; using medium resolution reduces the signal by a factor of 15. Even though
Mg(OH)$_2$ co-precipitation significantly lowers the matrix load of the seawater
samples, elements that potentially interfere with Cd isotopes, such as Mo, Sn and Pt,
are precipitated along with Cd and need to be monitored. Standards were measured
for mass bias and oxide corrections. Two standard solutions were used: 1) a 1 ppb
“Alfa Cd Zürich” Cd standard (Ripperger and Rehkämper, 2007b), the isotopic
composition of which is known accurately and precisely and is very similar to that of
the bulk silicate Earth (Table 2); 2) “Ryder06”, an in-house standard of seawater from
Ryder Bay that has undergone the sample preparation procedures, and therefore represents an unspiked version of the samples. Each sample was bracketed with a blank, and the “Alfa Cd Zürich” Cd standard was run every 3 samples. The standard “Ryder06” was spiked with various amounts of In, Mo and Cd to obtain signal corrections within a matrix similar to that of the samples (see below for details). It was also measured at the beginning of each run without any additives to test the validity of the blank and oxide corrections on the Cd signals discussed below.

The ion beam intensities of $^{110}$Cd, $^{111}$Cd, $^{112}$Cd, $^{114}$Cd were measured and $^{106}$Pd, $^{95}$Mo, $^{98}$Mo and $^{118}$Sn were monitored for interference corrections. Analytical conditions are listed in Table 3. An extended E-Scan range of 30% was used, which allowed rapid scanning without magnet jumps, hence a more efficient duty cycle and better precision. The tuning of the instrument was optimised for maximum Cd intensity and low oxide formation rates. Molybdenum oxides provided the most significant polyatomic interferences (Table 4), with $^{98}$Mo$^{16+}/^{98}$Mo$^+$ values of 0.07-0.10%.

Further corrections were made by assessing the interferences on standards before the samples were measured. A solution of “Ryder06” that had been spiked with 10 ppm Mo was measured prior to each run to assess MoO$^+$ formation. A pure Mo standard was measured before each run to determine mass bias corrections for MoO compounds that were not measured in the actual sample run (such as $^{94}$MoO$^+$ and $^{96}$MoO$^+$); these interferences were then corrected using either $^{95}$Mo or $^{98}$Mo count rates. $^{114}$Cd and $^{112}$Cd were corrected for $^{114}$Sn and $^{112}$Sn by measuring $^{118}$Sn and using the natural $^{114}$Sn/$^{118}$Sn and $^{112}$Sn/$^{118}$Sn ratios, respectively.
Pd interference on $^{110}$Cd was corrected by monitoring $^{106}$Pd after Mo and Sn corrections, and after correcting $^{106}$Pd for $^{106}$Cd based on $^{111}$Cd signals as follows (Equations 1-2):

$$^{110}\text{Cd}_{\text{corr}} = ^{110}\text{Cd} - ^{106}\text{Pd}_{\text{corr}} / A_{106\text{Pd}} \times A_{110\text{Pd}}$$

(1)

$$^{106}\text{Pd}_{\text{corr}} = ^{106}\text{Cd} - ^{111}\text{Cd} / A_{111\text{Cd}} \times A_{106\text{Cd}}$$

(2)

where $A_x$ = natural abundance if isotope, and the superscript * denotes count rates corrected for blank and MoO contributions.

The strong matrix effect of the sample solutions (about 1000 ppm each of Mg and Na) obtained by co-precipitation samples results in a suppression of the instrument blank signal. This suppression, and so the true instrument blank, was assessed by measuring the intensity of an In spike added to both 2% HNO$_3$ and the in-house standard ‘Ryder06’ standard and then applying Equation 3:

$$B = \frac{\text{In}_{\text{Ryder06}}}{\text{In}_{2\%}} \times B_{2\%}$$

(3)

where \(\text{In}_{\text{Ryder06}}\) = In intensity in Ryder06

\(\text{In}_{2\%}\) = In intensity in 2% acid

\(B_{2\%}\) = Machine blank for 2% acid

Blank contributions were about 5% of the signal for all Cd isotopes except $^{112}$Cd ca. 40%. Mass bias ($\Delta_M$) was corrected by measuring the isotope ratio of a 1 ppb solution of “Alfa Cd Zürich” and applying Equation 4:
\[ \Delta_{M} = \frac{\left[ \frac{^{110}Cd}{^{114}Cd} \right]_{\text{measured}}}{\left[ \frac{^{110}Cd}{^{114}Cd} \right]_{\text{ref}}} - 1 \]  

The natural sample ratio (or the ratio of the in-house Ryder06 standard) may not be exactly equal to the ratio of the Alfa Cd Zürich standard. Natural Cd isotopic fractionation in seawater occurs as a result of closed system biological uptake and ranges from \( \varepsilon^{114/110} \text{Cd} = \pm 3 \) to \( \pm 36 \) (Ripperger et al., 2007). However, the greatest fractionations occurs in Cd-depleted surface waters in the North Pacific ([Cd] ~ 0.003 nmol kg\(^{-1}\)). The [Cd] concentration of the Ryder Bay surface waters are higher, suggesting a lower degree of Cd isotopic fractionation, and are replenished regularly by deep water (\( \varepsilon^{114/110} \text{Cd} = \pm 3.3 \pm 0.5 \); (Ripperger et al., 2007)). Hence, the maximum error associated with assuming \( \varepsilon^{114/110} \text{Cd} = 0 \) is approximately 0.03%.

The external reproducibility of the isotope analysis was established by repeat measurements of unspiked standard “Ryder06”, and was found to be approximately 2% (Figure 3). The reproducibility for spiked samples should be as good as or better than 2% due to the greater proportion of \(^{110}\text{Cd} \). The accuracy of the isotope dilution method was determined based on duplicate measurements of the reference standard NASS-5, which yielded concentrations of 0.0221 ± 0.0004 (~2%) and 0.021 ± 0.006 (~30%) ppb using \(^{110}\text{Cd}/^{114}\text{Cd} \) and \(^{110}\text{Cd}/^{111}\text{Cd} \) respectively (certified value 0.023 ± 0.003; measured as 0.02224 ± 0.00004 by double spiked isotope dilution, (Ripperger and Rehkämper, 2007b)). \(^{110}\text{Cd}/^{114}\text{Cd} \) and \(^{110}\text{Cd}/^{111}\text{Cd} \) agree well for the samples (Figure 4), but due to the greater precision on the former ratio, only concentrations determined via \(^{110}\text{Cd}/^{114}\text{Cd} \) ratios are quoted in the results section.
Macronutrients were measured using a Skalar Autoanalyser (Kirkwood, 1996). The detection limit for NO$_3^-$, PO$_4^{3-}$ and Si analyses were 0.1, 0.05 and 0.1 $\mu$mol l$^{-1}$ respectively. The percentage error for all nutrient analyses was less than 5% relative to Ocean Scientific International (U.K.) standards. This results in a propagated error of ~5.5% on Cd/PO$_4^{3-}$ values.

4 Results and discussion

Our time series shows a consistent pattern of biological utilisation, with seasonal depletion in macronutrients NO$_3^-$ and PO$_4^{3-}$ during periods of high biomass (Figure 5). Cd co-varies with macronutrients (using all available data, Cd versus PO$_4^{3-}$, $r^2 = 0.70$, n = 18) with depletions occurring during the peaks of the summer bloom. However, the relationship between total chlorophyll $a$ (chl $a$) and both macronutrients and Cd is not statistically significant ($r^2 < 0.1$ for chl $a$ versus Si(OH)$_4$, PO$_4^{3-}$, NO$_3^-$ and Cd). This suggests that chl $a$, a measure of biomass, may not in this situation provide a reliable measure of nutrient utilisation per se. This could be because 1) phytoplankton utilise a range pigments in addition to chl $a$; 2) biomass does not relate to total nutrient drawdown because of grazing and remineralisation processes; 3) abiological/physical factors, such as storminess and water column mixing, influence the distribution of nutrients (Clarke et al., 2008).
4.1 Comparison between open ocean and coastal Cd/PO$_4^{3-}$: implications for Southern Ocean chemistry

The “global relationship” between Cd and P reflects various interactions between mixing of water masses containing different preformed nutrients and surface water biological fractionation. The non-linear nature of the relationship is not fully understood and may be a result of several different mechanisms (Cullen, 2006). The new Cd and PO$_4^{3-}$ data from Ryder Bay presented here (Figure 5, 6) are consistent with other published coastal datasets and appear offset towards higher Cd/P compared to the global open ocean trend (Frew, 1995; Jones and Murray, 1984; Van Geen and Luoma, 1993). Here, we suggest the Cd/PO$_4^{3-}$ of a parcel of surface seawater is determined by the initial Cd/PO$_4^{3-}$, set by inputs from upwelling and terrestrial runoff, and the subsequent fractionation trajectory of biological utilisation. The initial offset towards higher Cd values in coastal regions is a result of input from continentally derived sediments and the high Cd/PO$_4^{3-}$ composition of upwelling water. The biological utilisation trajectory in these coastal regions follows a curve with reduced uptake of Cd with respect to PO$_4^{3-}$ compared to open ocean regions (Figure 6). Variability in the extent of such enrichment in Cd over that expected for a given PO$_4^{3-}$ concentration is most likely to relate to spatial variation in the micronutrient content of the water column due to variations in upwelling, phytoplankton nutrient requirements and community structure.

4.1.1 Initial Cd/PO$_4^{3-}$ of upwelling water: continental input and water mass mixing

The most likely sources of high Cd/P inputs to our coastal setting are continental shelf sediments and terrestrial runoff from glaciers. Coastal and Continental Shelf Waters
(CCSW) contain higher Fe and Al inputs as a result of shelf sediment remineralisation and terrestrial input (Measures, pers. com.). In contrast to Fe and Al, Cd precipitates from porewaters and becomes concentrated in reducing sediments (Gobeil et al., 1997). However, in oxic layers at the sediment-water interface, the decomposition of organic matter can release Cd, which is largely mobile (Nolting et al., 1999). The surface layers of Antarctic continental sediments are generally organic rich and oxygenated, and these sediments, possibly with direct input from glacial runoff, will be a significant source of Cd to seawater.

We can assess the influence of these high Cd/PO$_4^{3-}$ coastal waters on the deep waters that emanate from the Weddell Sea using a mixing model of endmember water masses. Antarctic Bottom Water (AABW) forms largely on the Antarctic continental shelf and shows a correspondingly high Cd/PO$_4^{3-}$ value. The upwelling of Circumpolar Deep Water (CDW), formed from a mixture of aged North Atlantic Deep Water (NADW) and AABW, can be observed in measurements of Cd and PO$_4^{3-}$ measurements from open ocean regions of the Southern Ocean (Figure 6). We can use a simple mass balance calculation to quantify the impact of shelf water on CDW. Assuming endmember compositions of NADW and CCSW have [Cd] of 0.3 and 0.8 nM and PO$_4^{3-}$ of 1.6 and 2.3 μM respectively (from Figure 6), Modern CDW can be explained by entrainment of shelf waters in a mixing ratio of 40:60 NADW:CCSW (Figure 6). This mixing ratio is also supported by the oxygen isotope signature of AABW and Weddell Sea waters (Frew et al., 1995) and a simple mass balance calculation based on salinity. Assuming NADW and CCSW have salinities of 34.9 and 34.6 psu respectively (Adkins et al., 2002; Clarke et al., 2008; Meredith et al.,
2008), then a 40:60 ratio of NADW:CCSW explains the Modern CDW salinity of 34.7 psu.

### 4.1.2 Biological fractionation

The subsequent biological fractionation of the mixed water upwelling to the surface in the Southern Ocean will depend on environmental conditions. In open ocean regions the fractionation of Cd with respect to P follows a simple fractionation trend given by Equation 6, where $C_d^T$ and $P^T$ are the total Cd and P available in the ocean, $C_d^{sw}$ and $P^{sw}$ is the concentration of Cd and P in seawater, and $\alpha_{Cd-P}$ is the fractionation factor as defined in Equation 5 (Elderfield and Rickaby, 2000).

\[
\alpha_{Cd-P} = \frac{\left(\frac{Cd}{P}\right)^{organic}}{\left(\frac{Cd}{PO_4^{3-}}\right)^{seawater}}
\]  

(5)

\[
C_d^{sw} = C_d^T / \left\{ \alpha_{Cd-P} \left( \frac{P_T}{PO_4^{3-}} - 1 \right) + 1 \right\}
\]  

(6)

In the CCSZ (e.g. this study and the Princess Elizabeth Trough, (Frew, 1995)), the relative requirements of Cd with respect to $PO_4^{3-}$ are diminished, $\alpha_{Cd-P}$ is reduced (Equation 7) and there is a stock of Cd that is not appear to be utilised ("Cd$_{xs}$").

\[
C_d^{sw} = (C_d^T - C_d^{xs}) / \left\{ \alpha_{Cd-P} \left( \frac{P_T}{PO_4^{3-}} - 1 \right) + 1 \right\} + C_d^{xs}
\]  

(7)
This reduction in relative Cd requirements in coastal regions with respect to the open ocean may be due to differences in the activity of metalloenzymes, such as CA. The activity of CA is affected by the availability of macronutrients (Wang and Dei, 2001), micronutrients (Cullen et al., 2003; Cullen and Sherrell, 2005; Sunda and Huntsman, 1998) and pCO$_2$ (Cullen and Sherrell, 2005). Coastal regions show depleted seawater CO$_2$ in summer compared to the open Southern Ocean, suggesting variations in pCO$_2$ cannot provide a mechanism to explain the observed seawater Cd/PO$_4^{3-}$ (Álvarez et al., 2002; Bakker et al., 1997; Gibson and Trull, 1999; Hoppema et al., 2000; Takahashi et al., 2002). Hence, the most likely explanation for the lower utilisation of Cd is that the higher micronutrient conditions in coastal waters influences CA activity, Cd requirements or uptake mechanisms. It has been postulated that the non-linear relationship between Cd and PO$_4^{3-}$ is a result of two different fractionation relationships between Cd and PO$_4^{3-}$ in Fe replete and deficient conditions (Cullen et al., 2003). Under high Fe conditions, Cd/P uptake into cellular material is reduced, possibly due to a competing Fe-Cd cellular transporter (Armbrust, 2004; Cullen, 2006). Furthermore, the substitution of Zn into the Cd-CA structure influences the enzyme activity, such that CA activity and Cd requirements vary with Zn concentrations in the ambient medium (Park et al., 2007; Xu et al., 2008).

In Fe and Zn deficient regions (e.g. Subantarctic Zone), uptake of Cd with respect to P follows a simple trend given by Equation 6 with a constant fractionation factor, $\alpha_{\text{Cd-P}} = 3.5$. In Fe and Zn replete conditions of the CCSZ (e.g. Table 5) uptake of Cd follows a trend with a lower fractionation factor ($\alpha_{\text{Cd-P}} = 2$; Figure 6). Phytoplankton grown under such conditions have lower Cd requirements (Cullen, 2006), which could
provide a mechanism behind the lower value of $\alpha_{\text{Cd:P}}$ in coastal waters. Further, competitive interaction between metals (Sunda and Huntsman, 1998) or biologically produced ligands (Lee et al., 1996) can modulate uptake of Cd. For example, production of metal-binding polypeptides, phytochelatins, is activated in cultured diatoms under high internal and external Cd concentrations (Lee et al., 1996). Increased production of phytochelatins under higher micronutrient conditions could explain the reduction in uptake of Cd in coastal zones.

### 4.2 Seasonal variability and population structure

Our data show some scatter about the linear relationship between Cd and $\text{PO}_4^{3-}$ in Ryder Bay (Figure 6), which reflects seasonal variations in seawater Cd/$\text{PO}_4^{3-}$ due to changes in diatom species composition and environmental conditions. Such population related variations may also influence large scale global cycling of macro- and micronutrients in seawater given the predictable geographical variation in plankton types and sizes.

Surface Cd/$\text{PO}_4^{3-}$ of Ryder Bay has an initial background of $\sim 0.4$-$0.5$ nmol/μmol (Figure 5). Although this estimate is based on approximate concentrations measured using standard addition, it agrees well with other Antarctic coastal regions, e.g. Deception Island $\sim 0.6$; Palmer Station 0.3-$0.35$; (Sañudo-Wilhelmy et al., 2002). These values are also similar to the upper estimates of Cd/$\text{PO}_4^{3-}$ for UCDW, 0.35-$0.5$ nmol/μmol (Lösch et al., 1998). This is consistent with coastal Antarctic seawater being influenced by high Cd/$\text{PO}_4^{3-}$ waters from upwelling UCDW (Meredith et al., 2004).
During the first bloom (Jan-Feb 2006), the Cd/PO$_4^{3-}$ ratio in seawater increases as the uptake of P increases proportionately more than Cd with growth rate. As the early bloom declines, both Cd and P are remineralised and replaced by upwelling water restoring the Cd/PO$_4^{3-}$ to near background levels. Growth rates increase again during the late bloom (Feb-Mar), resulting in an increase in Cd/PO$_4^{3-}$.

Cd requirements are lower with respect to PO$_4^{3-}$ (i.e. Cd/PO$_4^{3-}$ is higher) for the late bloom than for the early bloom, which may reflect differences in community structure or environmental conditions, such as changes in photoperiod and temperature. Macro- and micronutrient requirements are a function of cell size (e.g. Ho et al., 2003) and, in particular, it is thought that smaller plankton have lower Cd uptake rates (Finkel et al., 2007) and greater PO$_4^{3-}$ requirements and uptake efficiencies (Asknes and Egge, 1991; Gligora et al., 2007; Wen et al., 1997). Indeed, in Ryder Bay, there is a greater contribution to surface productivity by smaller pico- and nanoplankton (<20 µm) with respect to microplankton (>20 µm) during the late summer bloom corresponding with higher Cd/PO$_4^{3-}$ (Figure 5). In addition to size, a shift in dominant phytoplankton community can also result in a shift in bulk community Cd requirements. Further, these requirements can change with environmental conditions to varying extents with different divisions. For example, laboratory cultures of diatoms show an increase in Cd requirements (and steady state influx of Cd with respect to PO$_4^{3-}$) with increasing temperature and irradiance; in contrast, cultures of cyanobacteria show a reduction in Cd uptake under similar conditions (Finkel et al., 2007). However, in this case although there is a change in cell size, there does not appear to be a major shift in the phytoplankton divisions throughout the summer with more than 55% of the population comprising diatoms. Preliminary population
analyses indicate there is a shift away from large centrics in the early summer towards smaller diatom species in the later bloom (Annett, pers. com.). In other words, these results show that a switch does not have to be between phytoplankton divisions during the bloom (e.g. diatoms to flagellates) in order to influence the seawater Cd/PO$_4^{3-}$ ratio but may be between phytoplankton genera within a division.

The variation in Cd requirements with respect to macronutrients with population and size structure in seawater may also influence the “global relationship” between Cd and PO$_4^{3-}$. For example, high nutrient upwelling zones favour the growth of microplankton (in particular diatoms) with high Cd requirements. Temperate open ocean regions favour the growth of other larger phytoplankton. Conversely, tropical oligotrophic gyres favour the growth of picoplankton and autotrophic bacteria with lower Cd requirements. Further, there is an effective microbial loop in these regions that results in more rapid regeneration, which may mask the effect of biological fractionation (Alvain et al., 2005; Follows et al., 2007).

4.3 Implications for glacial-interglacial reconstructions

We have shown the non-linear relationship between Cd and PO$_4^{3-}$ in seawater can be explained by a combination of 1) water mass mixing; 2) differential biological fractionation due to variation in micronutrient concentration, and 3) changes in phytoplankton community structure. These processes are likely to change on glacial-interglacial timescales, due to shifts in deep water formation processes and atmospheric inputs, resulting in long-term changes in the Cd/PO$_4^{3-}$ ratio of Southern Ocean seawater.
1) Deep water formation processes

Currently, Atlantic Sector Southern Ocean deep water originates in the southern region of the Weddell Sea near the continental shelf. Hence, these waters are replete in micronutrients and Cd utilisation is lower than open ocean conditions, which results in a relatively high seawater Cd/PO$_4^{3-}$. However, benthic foraminifera stable isotopes have been used to infer a shift in the deep convection site during the last glaciation to the northern rim of the Weddell Sea because the ice sheet was pinned to the edge of the continental shelf (Mackensen et al., 1996; Mackensen et al., 2001). Consequently, the site of deep water formation may have had lower inputs of micronutrients and, thus, surface waters may have experienced higher Cd utilisation and a lower seawater Cd/PO$_4^{3-}$. Such a shift in deep water convection could have lowered the Cd inventory of Southern Atlantic deep waters, explaining, in part, the conflict between foraminiferal $\delta^{13}$C and Cd/Ca data from the Southern Ocean LGM (Mackensen, 2001 and references therein).

2) Atmospheric inputs

A range of ice-core, terrestrial and marine records indicate an increase in dust supply to the Southern Ocean during the last glaciation (Kohfeld and Harrison, 2001; Petit, 1999). Although the link between biological productivity and atmospheric supply of micronutrients is poorly constrained and somewhat controversial (e.g. Maher and Dennis, 2001), it is possible that phytoplankton may have experienced Fe and Zn replete conditions in the Southern Ocean during the Last Glacial Maximum (LGM). Indeed, one model suggests that, although global dust deposition may not have increased dramatically, hydrological factors amplify the sensitivity of high latitude...
regions to dust input resulting in over an order of magnitude enhancement in Fe supply (Ridgwell and Watson, 2002). This would suggest growth conditions in the LGM open Southern Ocean could have been analogous to the modern coastal system, with lower Cd fractionation with respect to PO$_4^{3-}$.

3) Phytoplankton community structure

Changes in ocean stratification and sea-ice cover can shift phytoplankton community structure (Abelmann et al., 2006; Arrigo, 1999) and, thus, changes in macro- and micronutrient requirements (Arrigo, 2005). However, lack of constraint on phytoplankton community structures over longer timescales further compounds the ability to reconstruct past ocean nutrient budgets.

Shifts in the preformed Cd/PO$_4^{3-}$ ratio of seawater, and changes in biological fractionation in Southern Ocean surface waters, could have significantly altered the relationship between Cd/Ca recorded in foraminiferal calcite and ambient phosphate concentrations. For example, Cd/Ca foraminiferal records have previously been interpreted as showing no change in PO$_4^{3-}$ utilisation in the Subantarctic, and a lower PO$_4^{3-}$ utilisation (5%) in the Antarctic during the LGM compared to today (35%; Elderfield & Rickaby, 2000). However, assuming that the open Southern Ocean at the LGM exhibited Cd/PO$_4^{3-}$ characteristics of modern coastal regions due to enhanced atmospheric input, the same records imply PO$_4^{3-}$ utilisation was higher in the LGM Subantarctic compared to today. Further, a similar calculation suggests PO$_4^{3-}$ utilisation in the Antarctic Zone was lower than today (approximately 20%) but declined less than previously calculated.
5 Summary and conclusions

We present a time series of Cd and macronutrient data from a coastal site adjacent to the West Antarctic Peninsula, which shows that Cd is taken up during periods of high biological productivity despite nearshore, micronutrient replete conditions. These Antarctic coastal waters show high Cd/PO$_4^{3-}$ and can impact the preformed nutrient content of seawater in the open Southern Ocean through deep water formation and mixing with water masses originating further north. We have demonstrated that the non-linear relationship between Cd and PO$_4^{3-}$ in seawater can be explained by a combination of 1) water mass mixing; 2) differential biological fractionation due to variation in micronutrient concentration, and 3) changes in phytoplankton community structure, which can vary within a season. These processes are likely to change on glacial-interglacial timescales, due to shifts in deep water formation processes and atmospheric inputs, resulting in long-term changes in the Cd/PO$_4^{3-}$ ratio of Southern Ocean seawater. An understanding these shifts in the preformed Cd/PO$_4^{3-}$ ratio of seawater, and changes in biological fractionation in Southern Ocean surface waters, could resolve discrepancies between benthic foraminiferal Cd/Ca records and other paleonutrient proxies.

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Figure 1: All seawater dissolved Cd and Dissolved Inorganic Phosphate (DIP) data for the global ocean (surface and deep waters in open symbols) for different ocean basins (Boyle et al., 1976; Bruland, 1980; Bruland & Franks, 1983; Danielsson et al., 1985; Sakamoto-Arnold et al., 1987; Hunter & Ho, 1991; Nolting & de Baar, 1994; Löscher et al., 1998; Fitzwater et al., 2000; Abe, 2001, 2002; Ellwood, 2004). Also included are data from semi-enclosed South China Sea (Chen et al., 2005). Deep water data shown in closed symbols from de Baar et al., (1994).
Figure 2: Map of study site off the West Antarctic Peninsula, with the RaTS site shown by the grey box.

Figure 3: External reproducibility of 1 ppb Alfa Zürich standard and in-house standard ("Ryder06") using A) $^{110}\text{Cd}/^{111}\text{Cd}$ and B) $^{110}\text{Cd}/^{114}\text{Cd}$. Error bars show internal precision ($\pm 1.3\%$).

Figure 4: Comparison of methods for the analysis of dissolved Cd in seawater samples of using two different isotope ratios for isotope dilution ($\pm 1\sigma$).

Figure 5: Pigment and nutrient concentrations from 15 m collected at the RaTS site from 2005-2006. A) Total chlorophyll a concentrations (grey square; B) size fractionated chl a (data courtesy of BAS); macronutrient concentrations C) nitrate (white triangles), D) silicic acid (black squares) and E) phosphate (white diamonds); micronutrient concentrations F) cadmium (measured by standard addition (SA; grey dots) and isotope dilution (ID; black circles) and G) Cd/PO$_4^{3-}$ (grey circles). N and P measurements carried out by Weston, UEA, and Carson, Edinburgh. All errors bars show $\pm 2\sigma$.

Figure 6: Fractionation of dissolved Cd and PO$_4^{3-}$ or DIP in Southern Ocean waters. Upwelling CDW (cyan dashed line) is formed from a mixture of NADW and AABW. Endmember compositions shown in the large cyan circles (de Baar and al, 1994; Elderfield and Rickaby, 2000; Frew, 1995; Westerlund and Ohman, 1991). The mixing of these water masses can be observed in measurements of Cd and P measurements in Subantarctic Zone Waters (SAW, black circles), Polar Front regions (PF, red circles) and Antarctic Zone Waters (AAW, green circles). In open water regions (e.g. Subantarctic Zone, black circles), fractionation of Cd with respect to P follows a simple fractionation trend given by Equation 6 with a constant fractionation factor, $\alpha_{\text{Cd}-P} = 3.5$. In coastal conditions in the (CCSW e.g. this study, dark blue circles and the Princess Elizabeth Trough, PET, yellow circles) there is 1) stock of Cd, Cd$_{xs}$, that is not utilised (Equation 7), and 2) a lower fractionation factor, $\alpha_{\text{Cd}-P} = 2.0$. Utilisation and decay of nutrients follow trajectories given by the grey arrows. Note that the Cd/PO$_4^{3-}$ of upwelling waters will depend on the depth of mixing due to the deeper regeneration cycle of Cd.
<table>
<thead>
<tr>
<th>Standard</th>
<th>Quoted concentration (ppb)</th>
<th>Measured concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>IAPSO K15</td>
<td>0.08-0.12</td>
<td>0.087 ± 0.010</td>
</tr>
<tr>
<td>NASS-5</td>
<td>*0.023 ± 0.003</td>
<td>0.024 ± 0.004</td>
</tr>
</tbody>
</table>

*Certified seawater reference material for trace metals, National Research Council Canada

Table 1: Cd analysis of reference seawater standards. Errors are ±2σ.

Table 2: Isotope ratios of standards (Ripperger and Rehkämper, 2007b). Uncertainties in brackets denote 2σ.

<table>
<thead>
<tr>
<th>Solution</th>
<th>[^{110}\text{Cd}/^{111}\text{Cd}]</th>
<th>[^{110}\text{Cd}/^{114}\text{Cd}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alfa Cd Zürich (lot 901463E)</td>
<td>0.977047 (50)</td>
<td>0.438564 (50)</td>
</tr>
<tr>
<td>Spike</td>
<td>72.7346 (5072)</td>
<td>79.4532 (5540)</td>
</tr>
</tbody>
</table>

Table 3: Analytical parameters of ICP-MS analysis

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Thermo Finnigan Element2 magnetic sector ICP-MS with Cetac ASX-100 autosampler</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isotopes measured</td>
<td>95, 98, 106, 110, 111, 112, 114, 118, all in Low Resolution mode</td>
</tr>
<tr>
<td>Scan parameters</td>
<td>mass window 5%, 400 samples/peak, segment duration 40 ms</td>
</tr>
<tr>
<td>E-Scan range</td>
<td>30%</td>
</tr>
<tr>
<td>Analysis time</td>
<td>4.00 min (10 runs × 73 passes)</td>
</tr>
<tr>
<td>Plasma power</td>
<td>1450 W</td>
</tr>
<tr>
<td>Sample gas</td>
<td>1.12 L/m</td>
</tr>
<tr>
<td>Sample uptake rate</td>
<td>ca. 100 µL/min</td>
</tr>
</tbody>
</table>

Table 4: Interferences on isotopes of cadmium, and mean percentage of the signal of each interference. The percent signal calculated as follows, and averaged for all samples measured:

% signal = (counts from interference at mass peak)/(total counts at mass peak) x 100.
<table>
<thead>
<tr>
<th>Region</th>
<th>[Fe] (nM)</th>
<th>[Zn] (nM)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palmer Station, WAP</td>
<td>4-6</td>
<td>4-5</td>
<td>(Sañudo-Wilhelmy et al., 2002)</td>
</tr>
<tr>
<td>King George Island, South Georgia</td>
<td>&gt; 40</td>
<td></td>
<td>(Prendez and Carrasco, 2003; Prendez et al., 1996)</td>
</tr>
<tr>
<td>Weddell Sea</td>
<td>1-6</td>
<td>3-5</td>
<td>(Westerlund and Ohman, 1991)</td>
</tr>
<tr>
<td>Terra Nova Bay, Antarctica</td>
<td>3.5</td>
<td>5</td>
<td>(Sañudo-Wilhelmy et al., 2002)</td>
</tr>
<tr>
<td>Open Southern Ocean</td>
<td>0.2-0.5</td>
<td>0.2-0.5</td>
<td>(Abollino et al., 1995; Löscher et al., 1997; Löscher et al., 1998; Martin et al., 1990)</td>
</tr>
</tbody>
</table>

Table 5: Fe and Zn concentrations of some regions in the Southern Ocean and coastal Antarctica.